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(54) Electrodes for fuel cells

(57) The invention relates to a porous electrode comprising a porous catalytic layer containing a particulate catalytically-active noble metal, particulate carbon and a polymeric binder and a porous metallic collector disposed on the electrolyte side of this layer. According to the invention the catalytic layer has a thickness of less than 80 micrometer and particles of the noble metal are situated on the surface of and/or in the pores of, a portion of the carbon particles. The remaining carbon particles are free of noble metal. The invention meets the need for an electrode with a substantially lower noble metal content, while substantially retaining efficiency, power density and simplicity of manufacture.

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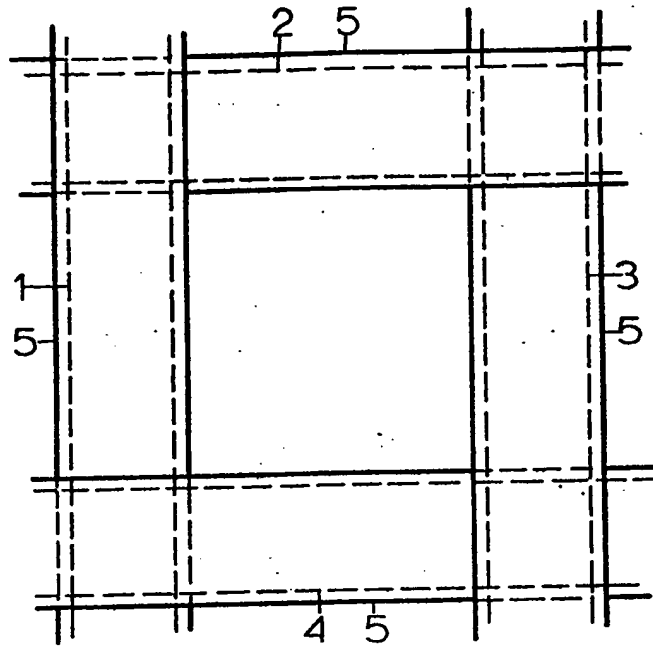


FIG.1

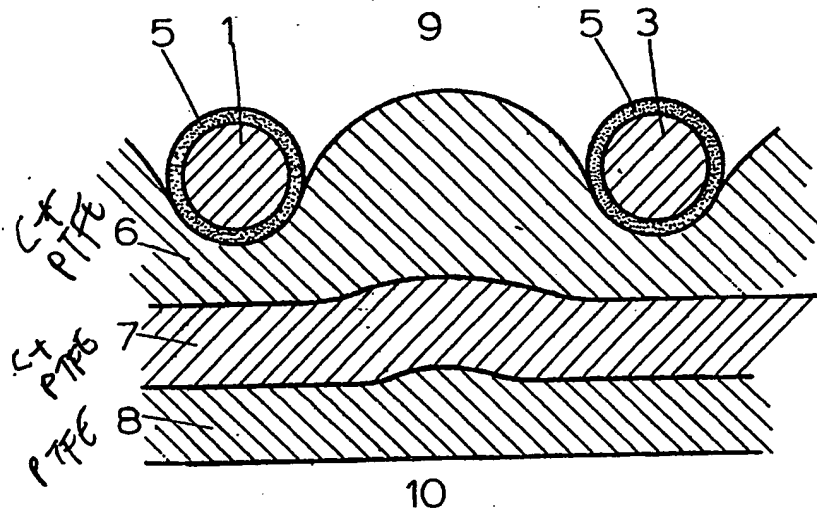


FIG. 2

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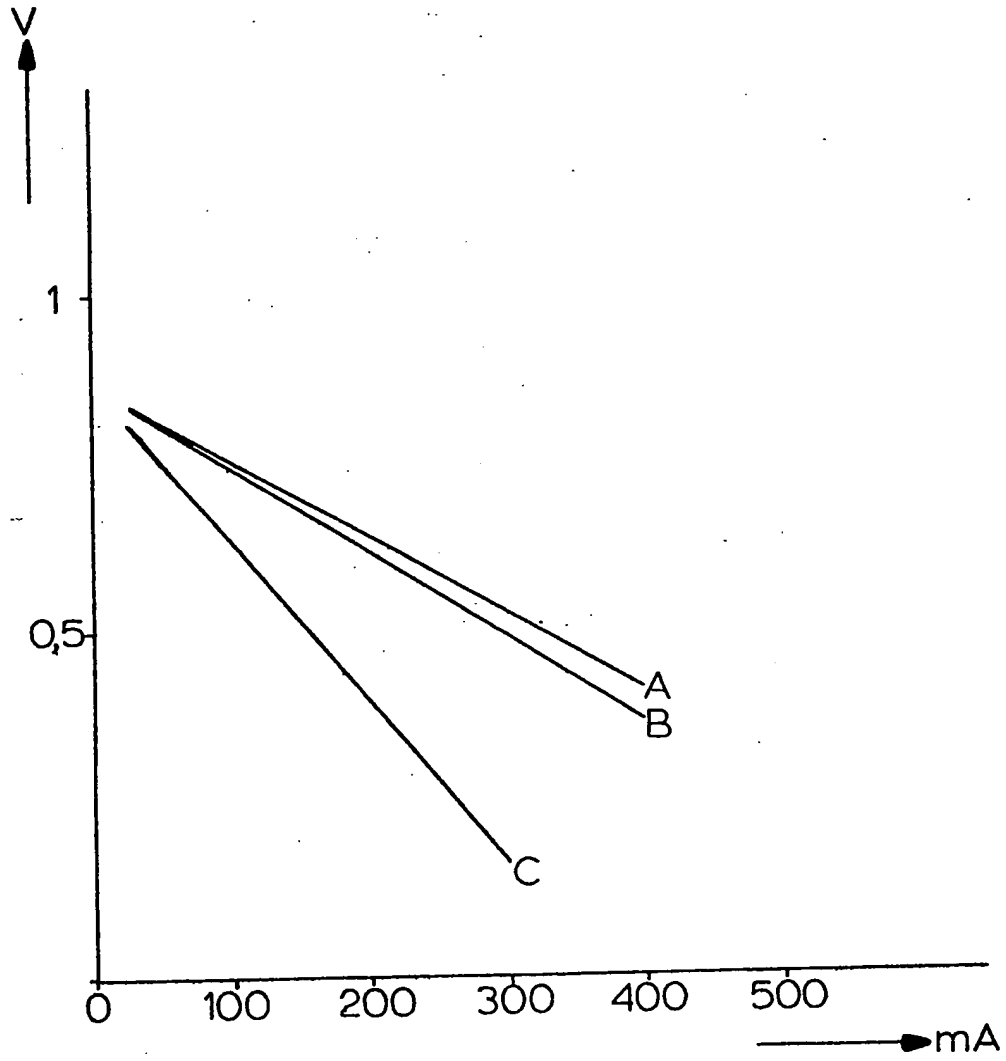


FIG.3

## SPECIFICATION

## Porous electrode

5 This invention relates to a porous electrode comprising a porous catalytic layer containing a particulate catalytically-active noble metal, particulate carbon and a polymeric binder, and a porous metallic collector disposed on the electrolyte side of the said catalytic layer, and also relates to electrochemical cells, e.g. fuel cells, containing such electrodes.

10 Such electrodes, which are particularly suitable for use in fuel cells, are described for example in the published Dutch Patent Application 7214900. When used in fuel cells the fuel used penetrates into the pores of the catalytic layer where it is converted with the production of electric current. The generation of the electric current takes place throughout the catalytic layer and the current generated is collected by the metallic collector from which it is removed and utilized. During operation the electrode is in contact with a suitable electrolyte which closes the circuit within the fuel cell and by which the products of reactions occurring at the cathode and anode can be discharged.

A disadvantage of such known electrodes lies in the amount of noble metal that is necessary for effective operation. For instance the known electrode contains 0.4 mg/cm<sup>2</sup> of platinum and palladium, which militates against large-scale application due to the present high costs of such noble metals. Such problems are described for example in the Report 'Elektrochemische Aspecten van de Energie-voorziening' by Stichting Nederlands Instituut voor Elektrowarmte en Elektrochemie NIVVE, 1975, pp. 62 and 63. According to this article, it was considered that reduction of the amount of noble metal in the electrode leads to lower efficiency and power density of the current produced.

40 The invention meets the need for an electrode with a substantially lower noble metal content while substantially retaining efficiency, power density and simplicity of manufacture.

The invention is based on the discovery that in 45 such electrodes, very thin catalytic layers containing considerably lower concentrations of noble metals than have hitherto been used, can effectively be used in fuel cells, provided that the noble metal particles are distributed over the carbon particles in a particular manner as hereinafter set forth. By this means the amount of noble metal component can be reduced by a factor of 10 or more without loss of performance of the electrode. According to a preferred feature of the invention the said catalytic layer 50 contains from 1 to 100 micrograms per sq. cm. of noble metal. An additional advantage of the electrode according to the invention is the considerably improved conduction of ions during operation.

The invention provides a porous electrode comprising a porous catalytic layer containing a particulate catalytically-active noble metal (as hereinafter defined), particulate carbon and a polymeric binder, and a porous metallic collector disposed on the electrolyte side of the said catalytic layer, characterized in that the catalytic layer has a thickness of less

than 80  $\mu$ m, and particles of the noble metal are situated on the surface of and/or in the pores of, a portion of the carbon particles, the remaining carbon particles being free of noble metal.

70 The term "noble metal" is hereby defined as one or more of the metals palladium, platinum, iridium, rhodium, silver and gold, or mixtures of two or more of such elements.

The preferred noble metals used in the invention 75 are platinum or palladium or a mixture thereof.

The catalytically active layer in the electrode according to the invention may be made particularly thin in an anode, in particular in a hydrogen electrode for a fuel cell burning hydrogen. For such 80 uses it preferably has a thickness of not more than 60  $\mu$ m, and particularly has a thickness of not more than 40  $\mu$ m.

Electrodes are known in which carbon particles present contain noble metal particles, and then 85 further carbon particles are applied as a means of improving the electron-conductivity (cf. US Patent 3,306,779 and French Patent 2,344,969). However the use of much thinner catalytic layers with comparable performance to known electrodes has not previously been described. Furthermore the possible use of lower noble metal concentrations, and the obtaining of substantially improved ion-conductivity during operation has not previously been known.

95 The catalytically-active metal is present as particles on and/or in, a portion of the carbon particles. It is essential that not all carbon particles contain metal particles. Preferably from 10 to 90% by weight of the carbon particles contain catalytically-active metal. It is possible for the metal particles to be distributed unevenly over the metal-containing carbon particles. For instance part of the carbon particles may contain a relatively high concentration of catalytically active metal and another part a lower concentration. The carbon type in the carbon particles with catalytically active metal may differ from the carbon type in the other carbon particles not associated with catalytically-active metal.

The polymeric binder may be any suitable resin, 110 particularly an apolar synthetic resin. Known resins suitable for this purpose are for example polyethylene, polypropylene, polyvinylchloride, and particularly polytetrafluoroethylene, which is the preferred binder.

115 The porosity of the catalytic layer may be uniform over the entire thickness of the porous layer, or it may increase or decrease, either continuously or stepwise, over the thickness.

The electrode comprises a porous metallic collector which may be for example a metal gauze with a wire thickness of about 150  $\mu$ m and a mesh width of approximately 700  $\mu$ m, or a perforated or an expanded metal plate of comparable dimensions.

The metal gauze of the collector may be made of 125 any suitable material, e.g. nickel or steel. The collector material may be surrounded by a contiguous collector coat of an electrically conducting resin or a mixture of resin and a conducting material, e.g. carbon, in order to inhibit corrosion of the collector.

130 For the correct operation of the electrode it is

important in use that the collector be situated on the electrolyte side of the catalytic layer. This has advantages also in the construction of the electrode.

5 The electrodes according to the invention may be made in any suitable way. For instance carbon containing a catalytically active metal and powdered binding material e.g. tetrafluoroethylene, and if so desired a pore former is pressed into an electrode at

10 elevated temperature, e.g. in a suitable mould, after which the pore former can be lixiviated, e.g. with hot water. Suitable pore formers are soluble salts, e.g. sodium sulphate, sodium carbonate and ammonium carbonate.

15 Using such a procedure it is advantageous first to make the catalytic layer and the collector separately and then to press the collector on the electrolyte side at least partly into the layer composition obtained. A very firm electrode with good porosity

20 properties is thus obtained. However the catalytic layer may also be formed in situ by deposition onto the collector.

In the electrodes according to the invention the layer that contains the catalyst and which is

25 sufficiently porous to allow gas and liquid to pass preferably adjoins a layer that is impervious to liquid, but pervious to gas. During operation the layer that is pervious to gas and liquid is then in contact with the electrolyte, e.g. a sodium-

30 hydroxide or potassium-hydroxide solution or a phosphoric-acid solution, and the layer that is pervious to gas only is in contact with the gas. At the anode the gas consists in the gaseous fuel, e.g. hydrogen. At the cathode the gas consists in oxygen or

35 a gas containing molecular oxygen, e.g. air.

#### *Example and comparative experiments*

This example illustrates the use of the invention in a gas-diffusion electrode. Reference is made to the diagrammatic Figures 1 and 2 of the accompanying drawings, of which:-

40 *Figure 1* is a top view of part of an electrode according to the invention; and

*Figure 2* shows a section normal to the electrode surface. The same numbers refer to the same parts.

45 The nickel or steel wires 1, 2, 3 and 4 form part of the collector gauze. Instead of wire gauze, a perforated nickel or steel plate, so-called expanded metal, may be used. The thickness of the wires is about 150  $\mu\text{m}$ , the porosity of the collector gauze

50 about 50%.

The term porosity as used here and hereinafter means the ratio between the volume taken up by the pores, or the volume not taken up by the particular material, and the volume of the layer concerned.

55 The collector wires are surrounded by a collector protection coat 5, which consists of an epoxy resin varnish Elastolux blank V2037 obtained under the Trade Mark ELASTOLUX containing 50% by weight (of the resin + graphite) of graphite particles. The

60 thickness of the layer is 15  $\mu\text{m}$ .

The coated collector wires are embedded in a porous layer made up of constituent layers 6, 7 and 8. When the electrode is in operation, the electrolyte phase is at 9. Some electrolyte will have penetrated

65 into the pores of the electrode. Furthermore when

the electrode is in operation the gaseous phase is at 10. In this example use is made of a gas mixture containing molecular oxygen, namely air. Layer 6 consists of a mixture of 90% by weight of carbon and 10% by weight of polytetrafluoroethylene. The polytetrafluoroethylene content may however

70 vary, but it should preferably be between 8 and 15% by weight. Layer 6 is approximately 40  $\mu\text{m}$  thick, but is less in the vicinity of collector wires 1 and 3.

75 The porosity of layer 6 is 30%, apart from the micropores that are present in the carbon particles and which are not important to the working of the electrode. Preferably it is between 25 and 35%. The pore width is 1 to 10  $\mu\text{m}$ . This porosity depends on the particle size of the carbon powder and the polytetrafluoroethylene powder used to make the layer and on the pressure used in making the electrode. The same applies to the porosities on the layers 7 and 8 still to be discussed.

85 Layer 7 is the catalytic layer and has a thickness of 40  $\mu\text{m}$ . It consists of a mixture of carbon particles without platinum, carbon particles containing 5% by weight of platinum, and polytetrafluoroethylene. The polytetrafluoroethylene content preferably is between 15 and 30% by weight, and is 21% by weight in this example. The porosity is 20% and preferably is between 20 and 25%. The carbon particles without platinum make up 7 to 75% by weight of layer 7, in this example 63% by weight.

95 The platinum content amounts to 27  $\mu\text{g}/\text{cm}^2$ .

Layer 8 is 180  $\mu\text{m}$  thick on an average and consists entirely of polytetrafluoroethylene. The average porosity is 50% and the pore width is between 1 and 10  $\mu\text{m}$ , just as in layers 6 and 7.

100 Two electrodes of this type were used as hydrogen electrode and as air electrode, respectively, in a hydrogen-air fuel cell. The electrolyte used was a 6.6 N aqueous potassium-hydroxide solution. The fuel cell operated at a pressure of 1 atmosphere and at 65°C. The current voltage curve is shown by Figure 3, Graph A. As shown by Figure 3, efficiency and power density were even better than those of a fuel cell with otherwise similar electrodes with a thickness of layer 7 of 120 m with evenly distributed

105 platinum metal in an amount of 400  $\mu\text{g}/\text{cm}^2$  (Graph B). A fuel cell with otherwise similar electrodes with a thickness of layer 7 of 40  $\mu\text{m}$  with evenly distributed platinum metal in an amount of 27  $\mu\text{g}/\text{cm}^2$  gave the current voltage curve shown in Figure 3 as

110 Graph C. This curve indicates a considerably poorer behaviour of the fuel cell.

#### CLAIMS

1. A porous electrode comprising a porous catalytic layer containing a particulate

120 catalytically-active noble metal (as hereinbefore defined), particulate carbon and a polymeric binder, and a porous metallic collector disposed on the electrolyte side of the said catalytic layer, characterized in that the catalytic layer has a thickness of less

125 than 80  $\mu\text{m}$ , and particles of the noble metal are situated on the surface of and/or in the pores of, a portion of the carbon particles, the remaining carbon particles being free of noble metal.

2. An electrode according to Claim 1, wherein the catalytically active metal is platinum, palladium, or

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a mixture thereof.

3. An electrode according to Claim 1 or Claim 2, wherein from 10% to 90% by weight of the carbon particles are associated with catalytically active

5 metal.

4. An electrode according to any of Claims 1 to 3, wherein the electrode is an anode.

5. An electrode according to Claim 4, wherein the electrode is a hydrogen electrode for a fuel cell  
10 burning hydrogen.

6. An electrode according to any of Claims 1 to 5, wherein the said catalytic layer contains from 1 to 100 micrograms per square cm. of noble metal.

7. An electrode according to any of Claims 1 to 6,  
15 wherein the catalytic layer has a thickness of not more than 40  $\mu\text{m}$ .

8. An electrode according to any of Claims 1 to 7, wherein the polymeric binder is an apolar synthetic resin.

20 9. An electrode according to Claim 8, wherein the polymeric binder is polytetrafluoroethylene.

10. An electrode according to Claim 1, substantially as hereinbefore described, with particular reference to the accompanying drawings.

25 11. An electrochemical cell containing one or more electrodes according to any of Claims 1 to 10.

12. An electrochemical cell as claimed in Claim 11, which is a fuel cell.